

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-055528

(43)Date of publication of application : 26.02.2003

(51)Int.Cl. C08L 53/00
C08J 3/24
C08L 23/22

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(54) THERMOPLASTIC ELASTOMER COMPOSITION**(57)Abstract:**

PROBLEM TO BE SOLVED: To obtain a new thermoplastic elastomer composition having high flexibility and excellent in moldability and processability, rubber characteristics, mechanical strength, permanent compression set property or vibration-damping property.

SOLUTION: This thermoplastic elastomer composition is obtained by compounding (A) an isobutylene-based block copolymer containing a polymer block mainly comprising isobutylene and a polymer block mainly comprising an aromatic vinyl-based compound with (B) an isobutylene-based polymer having an alkenyl group at the end and optionally (C) a reinforcing material which is at least one kind of polymer selected from polystyrenes and polyphenylenes.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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CLAIMS

[Claim(s)]

[Claim 1] The thermoplastic-elastomer constituent which comes to blend the isobutylene system block copolymer (A) containing the polymer block which makes a subject the polymer block and aromatic series vinyl system compound which make an isobutylene a subject, and the isobutylene system polymer (B) which has an alkenyl radical at the end [claim 2] The isobutylene system polymer (B) which has an alkenyl radical at the end is a thermoplastic-elastomer constituent according to claim 1 with which an allyl group is introduced into an end by the substitution reaction of an allyl compound trimethyl silane and the chlorine of an isobutylene system polymer end.

[Claim 3] The thermoplastic-elastomer constituent according to claim 1 or 2 with which a thermoplastic-elastomer constituent constructs a bridge dynamically in an isobutylene system block copolymer (A) and the isobutylene system polymer (B) which has an alkenyl radical at the end at the time of melting kneading of an isobutylene system polymer (B) which has an alkenyl radical at the end.

[Claim 4] The thermoplastic-elastomer constituent according to claim 1 or 2 characterized by the isobutylene system polymer (B) which has an alkenyl radical at the end constructing a bridge beforehand before being mixed with an isobutylene system block copolymer (A).

[Claim 5] from the polymer block (a) with which the block which constitutes an isobutylene system block copolymer (A) makes an isobutylene a subject, and the polymer block (b) which makes an aromatic series vinyl system compound a subject — becoming — (b)-(a) — the thermoplastic-elastomer constituent according to claim 1 to 4 which is the triblock copolymer in which the structure of (b) is shown.

[Claim 6] The thermoplastic-elastomer constituent according to claim 1 to 5 which furthermore contains reinforcing materials (C).

[Claim 7] The thermoplastic-elastomer constituent according to claim 6 with which reinforcing materials (C) are chosen from polystyrene and polyphenylene ether and which is a kind at least.

[Claim 8] The thermoplastic-elastomer constituent according to claim 1 to 7 which furthermore contains a cross linking agent (D).

[Claim 9] The thermoplastic-elastomer constituent according to claim 8 whose cross linking agent (D) is a hydrosilyl radical content compound.

[Claim 10] The thermoplastic-elastomer constituent according to claim 1 to 9 characterized by carrying out 10-300 weight section content of the isobutylene system polymer (B) with which the alkenyl radical was introduced into the end to the isobutylene system block-copolymer (A) 100 weight section.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is rich in flexibility and relates to the new thermoplastic-elastomer constituent excellent in fabrication nature, the rubber-property, the mechanical strength, and the compression set property.

[0002]

[Description of the Prior Art] Conventionally, what blended the cross linking agent, the reinforcing agent, etc. with rubber, such as natural rubber or synthetic rubber, and constructed the bridge under elevated-temperature high pressure as polymeric materials which have elasticity is used widely. However, with such rubber, the stroke which performs bridge formation and shaping over long duration under elevated-temperature high pressure is required, and it is inferior to workability. Moreover, since the rubber which constructed the bridge does not show thermoplasticity, generally recycle shaping is impossible for it like thermoplastics. Therefore, the thermoplastic elastomer which can manufacture a cast easily like usual thermoplastics using general-purpose melting forming technique, such as heat press forming, injection molding, and extrusion molding, is developed variously in recent years. Moreover, the elasticity vinyl chloride compound is used widely as an ingredient which has flexibility. Although this is used for various applications as a flexible ingredient at the room temperature, the alternative with other ingredients is demanded from the demand of the formation of devinyl chloride in recent years. The thermoplastic-elastomer constituent is used as alternate material for this. The polymer of various formats, such as current, an olefin system, an urethane system, an ester system, a styrene system, and a vinyl chloride system, is developed and marketed by such thermoplastic elastomer.

[0003] A styrene thermoplastic elastomer is rich in flexibility, and excellent in good rubber elasticity with ordinary temperature. [among these] As a styrene thermoplastic elastomer, the styrene-butadiene-styrene block copolymer (SBS), the styrene-isoprene-styrene block copolymer (SIS), a styrene-ethylene butylene-styrene block copolymer (SEBS), a styrene-ethylene propylene-styrene block copolymer (SEPS) that hydrogenated them, etc. are developed. However, these block copolymers had the inadequate compression set property.

[0004] The isobutylene system block copolymer which contains the polymer block which makes an isobutylene a subject, and the polymer block which makes an aromatic series vinyl system compound a subject as thermoplastic elastomer which was rich in flexibility, was excellent in good rubber elasticity on the other hand with ordinary temperature, and was further excellent in gas barrier nature and sealing performance is known. However, this isobutylene system block copolymer also had a problem in the pressurization reduction of area at the time of heating (compression set), or the rubber elasticity at the time of an elevated temperature.

[0005] Moreover, the thermoplastic polymerization body composition object which consists of the isobutylene system block copolymer and the bridge formation object of rubber containing the polymer block which makes an isobutylene a subject is known (re-official announcement patent WO 98/14518). This constituent was insufficient, although the compression set property has been improved and the compression set has been improved.

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block (a) which makes a subject the isobutylene in an isobutylene system block copolymer (A), and an aromatic series vinyl compound. Although there is especially no limit, the polymer block (a) which makes an isobutylene a subject from the balance of physical properties and workability 95 - 20 weight section. It is desirable that the polymer block (b) which makes an aromatic series vinyl compound a subject is 5 - 80 weight section. It is desirable that the polymer block (b) whose polymer block (a) which makes an isobutylene a subject makes a subject 90 - 60 weight section and an aromatic series vinyl compound is especially 10 - 40 weight section.

[0015] Moreover, the structure which consists of at least one of the polymer blocks (a) which make an isobutylene a subject from the point of the physical properties of the constituent obtained and workability, and at least two of the polymer blocks (b) which make an aromatic series vinyl system compound a subject as desirable structure of the isobutylene system block copolymer (A) of this invention is desirable. the above - structure - ***** - especially - a limit - there is nothing - although - for example - (---b---) - (---a---) - (---b---) - from - forming - having - a triblock - a copolymer - [---(b---)---(a---)---(b---)] - a unit - a repeat - having - multi - a block copolymer - and - (---b---) - the jib which consists of (a) - at least one sort chosen from the star-like polymer which uses a lock copolymer as an arm can be used. furthermore, the polymer which makes an isobutylene a subject into an isobutylene system block copolymer (A) in addition to the above-mentioned structure, the polymer which makes an aromatic series vinyl system compound a subject, and (a)- the jib which consists of (b) - at least one sort of a lock copolymer may be contained. at least one of the polymer blocks (a) which make a subject the isobutylene contained in an isobutylene system block copolymer (A) from the point of physical properties and workability, and at least two [however,] of the polymer blocks (b) which make an aromatic series vinyl system compound a subject - since - it is desirable that the thing of the becoming (b)-(a)-(b) structure becomes 50% of the weight or more.

[0016] Although there is especially no limit also in the weight average molecular weight of an isobutylene system block copolymer (A), 30,000-500,000 are desirable, and 40,000 to especially 400,000 is good ****. The fall of a moldability etc. is large when a mechanical property etc. is not fully discovered when weight average molecular weight is less than 30,000, and exceeding 500,000. The isobutylene system polymer (B) as used in the field of this invention which has an alkenyl radical at the end means the block with which an isobutylene occupies 90 % of the weight or more preferably 70% of the weight or more 50% of the weight or more. Although monomers other than an isobutylene in the isobutylene system polymer (B) which has an alkenyl radical at the end will not be limited especially if they are monomer components in which cationic polymerization is possible, they can illustrate monomers, such as dienes, such as aromatic series vinyl, aliphatic series olefins, an isoprene, a butadiene, and a divinylbenzene, vinyl ether, and beta-pinene. These may be used independently, and two or more sorts may be combined and they may be used.

[0017] Although there is especially no limit in the number average molecular weight of the isobutylene system polymer (B) which has an alkenyl radical at the end, 1,000-500,000 are desirable and 2,000 to especially 100,000 is desirable. When a mechanical property etc. is not fully discovered when number average molecular weight is less than 1,000, and exceeding 500,000, while the fall of a moldability etc. is large, the improvement effect of a compression set becomes small.

[0018] It will not be restricted especially if the alkenyl radical of this invention is a radical including the carbon-carbon double bond which has activity to the crosslinking reaction of the (B) component for attaining the purpose of this invention. As an example, ring type unsaturated hydrocarbon radicals, such as aliphatic series partial saturation hydrocarbon groups, such as a vinyl group, an allyl group, a methyvinyl radical, a propenyl radical, a butenyl group, a pentenyl radical, and a hexenyl radical, a cyclo propenyl radical, a cyclo butenyl group, a cyclo pentenyl radical, and a cyclohexenyl group, can be mentioned. The approach of making the compound which has a partial saturation radical react to the polymer which has functional groups, such as a hydroxyl group which is indicated by JP.3-152184A and JP.7-304909A as the introductory approach of the alkenyl radical to the end of the isobutylene system polymer of this invention,

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[0006]

[Problem(s) to be Solved by the Invention] In view of the technical problem of the above-mentioned conventional technique, the purpose of this invention is rich in flexibility, and is to offer the thermoplastic-elastomer constituent excellent in fabrication nature, the rubber-property, the mechanical strength, and the compression set property.

[0007]

[Means for Solving the Problem] That is, this invention is a thermoplastic-elastomer constituent which comes to blend the isobutylene system block copolymer (A) containing the polymer block which makes a subject the polymer block and aromatic series vinyl system compound which make an isobutylene a subject, and the isobutylene system polymer (B) which has an alkenyl radical at the end. The isobutylene system polymer (B) which has an alkenyl radical at said end has that desirable by which the allyl group was introduced into the end by the substitution reaction of an allyl compound trimethyl silane and the end chlorine of an isobutylene system polymer. Moreover, as a thermoplastic-elastomer constituent, a bridge can be dynamically constructed in an isobutylene system block copolymer (A) and the isobutylene system polymer (B) which has an alkenyl radical at the end at the time of melting kneading of an isobutylene system polymer (B) which has an alkenyl radical at the end, and the isobutylene system polymer (B) which has an alkenyl radical at the end can also construct a bridge beforehand, before being mixed with an isobutylene system block copolymer (A).

[0008] from the polymer block (a) with which the block which constitutes said isobutylene system block copolymer (A) carried out as structure of a block copolymer makes an isobutylene a subject, and the polymer block (b) which makes an aromatic series vinyl system compound a subject - becoming - (b)-(a)- it is desirable that it is the triblock copolymer in which the structure of (b) is shown.

[0009] As a thermoplastic-elastomer constituent, reinforcing materials (C) can be contained further and a cross linking agent (D) can also be contained further.

[0010]

[Embodiment of the Invention] The thermoplastic-elastomer constituent of this invention is a thermoplastic-elastomer constituent which comes to blend the isobutylene system block copolymer (A) containing the polymer block which makes a subject the polymer block and aromatic series vinyl system compound which make an isobutylene a subject, and the isobutylene system polymer (B) which has an alkenyl radical at the end.

[0011] The polymer block which makes a subject the isobutylene of the isobutylene system block copolymer (A) of this invention means the block with which an isobutylene occupies 90 % of the weight or more preferably 70% of the weight or more 50% of the weight or more. Although monomers other than an isobutylene under polymer block which makes an isobutylene a subject will not be limited especially if they are monomer components in which cationic polymerization is possible, they can illustrate monomers, such as aromatic series vinyl, aliphatic series olefins, dienes, vinyl ether, and beta-pinene. These may be used independently, and two or more sorts may be combined and they may be used.

[0012] The polymer block which makes a subject the aromatic series vinyl system compound of an isobutylene system block copolymer (A) means the block with which an aromatic series vinyl system compound occupies 90 % of the weight or more preferably 70% of the weight or more 50% of the weight or more. Although there will be especially no limit if it is the monomer in which cationic polymerization is possible as monomers other than the aromatic series vinyl compound under polymer block which makes an aromatic series vinyl system compound a subject, monomers, such as aliphatic series olefins, dienes, vinyl ether, and beta-pinene, can be illustrated.

[0013] As an aromatic series vinyl system compound, styrene, alpha methyl styrene, beta-methyl styrene, p-methyl styrene, t-butyl styrene, monochlorostyrene, dichloro styrene, methoxy styrene, an indene, etc. are mentioned. Also in the above-mentioned compound, styrene, alpha methyl styrene, p-methyl styrene, and an indene are desirable from the balance of cost, physical properties, and productivity, and you may also choose two or more sorts from them.

[0014] It is related with the rate of the polymer block (b) which makes a subject the polymer

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and introducing a partial saturation radical into a polymer is mentioned. Moreover, the method of performing the further aforementioned alkenyl radical installation reaction in order to introduce a partial saturation radical into the polymer which has a halogen atom, after performing the Friedel Crafts reaction with the approach and the various phenols which perform a substitution reaction with the approach of performing a Friedel Crafts reaction with alkenyl phenyl ether, a bottom allyl compound of Lewis acid existence trimethyl silane, etc. and introducing a hydroxyl group etc. is mentioned. It is also possible to introduce a partial saturation radical at the time of the polymerization of a monomer as furthermore indicated by U.S. Pat. No. 4316973, JP.63-105005A, and JP.4-288309A.

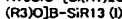
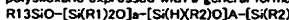
[0019] Moreover, as for the alkenyl radical permuted by the end, it is desirable that 0.5 pieces exist in at least 0.2 ends still more preferably per molecule. When fewer than this, the constituent excellent in the compression set is not obtained.

[0020] Or the thermoplastic-elastomer constituent which consists of an isobutylene system block copolymer (A) and an isobutylene system polymer (B) with which the alkenyl radical was introduced into the end would not construct a bridge dynamically at the time of melting kneading. its constituent the constituent which constructed the bridge beforehand in the isobutylene system polymer (B) with which the alkenyl radical was introduced into the end, and carried out melting mixing of the isobutylene system block copolymer (A) further carried out [the constituent] dynamic bridge formation especially preferably is desirable.

[0021] In the rack abutment formed here, the object with which (B) constructed the bridge independently, and the object with which (A) and (B) were contained in the rack abutment, and constructed the bridge over coincidence is contained. It is desirable to form a bridge formation object by the (B) independent among these.

[0022] Although a well-known approach can be used as a means to construct a bridge in the isobutylene system polymer (B) with which the alkenyl radical was introduced into the end and there is especially no limit, radical crosslinking can also be performed, for example without using the heat bridge formation by heating, the bridge formation by the cross linking agent (D), or a cross linking agent.

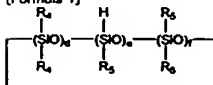
[0023] It is desirable to use a hydrosilyl radical content compound as a cross linking agent (D) for obtaining the bridge formation object of the isobutylene system polymer (B) with which the alkenyl radical was introduced into the end of this invention. As a hydrosilyl radical content compound, there is especially no limit and it can use various kinds of things. Namely, chain-like polysiloxane expressed with a general formula (I) or (II):



(As for R1 and R2, the alkyl group of carbon numbers 1-8 or a phenyl group, and R3 show the alkyl group or aralkyl radical of carbon numbers 1-10 among a formula.) a shows the integer with which $0 < a < 100$ and b fills $2 < b < 100$, and c fills $0 < c < 100$. Cyclosiloxane expressed with a general formula (III):

[0024]

[Formula 1]



(11)

[0025] (As for R4 and R5, the alkyl group of carbon numbers 1-8 or a phenyl group, and R6 show the alkyl group or aralkyl radical of carbon numbers 1-10 among a formula.) $0 < d < 8$ and e express $2 < e < 10$, and f expresses the integer of $0 < f < 8$, and d fills $3 < d + f < 10$, etc. - a compound can be used. What compatibility with the (B) component is especially expressed with the following general formula (IV) to from the point of being good, among the compounds which

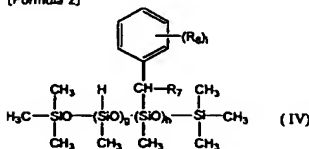
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have the further above-mentioned hydrosilyl radical (Si-H radical) is desirable.

[0026]

[Formula 2]



[0027] (Among a formula, g and h are integers and are 2 <= g <= 50, 2 <= h, and 0 <= h) R7 may express a hydrogen atom or a methyl group, and R8 may have one or more rings by the hydrocarbon group of carbon numbers 2-20. i is the integer of 0 <= i <= 5.

Although the isobutylene system polymer (B) and cross linking agent by which the alkenyl radical was introduced into the end are mixable at a rate of arbitration, it is desirable that the mole ratio of an alkenyl radical and a hydrosilyl radical is in the range of 0.2-5 from the field of hardenability, and it is still more desirable that it is especially 0.2-5, if a mole ratio becomes five or more, bridge formation is inadequate, if smaller than constituent profit *** with reinforcement of enough, and 0.2, since an activity hydrosilyl radical remains in large quantities into a constituent, after bridge formation will be uniform, and a constituent with reinforcement will not be obtained.

[0028] Although the crosslinking reaction of a polymer (B) and a cross linking agent (D) advances by mixing and heating two components, in order to advance a reaction more quickly, it can add a hydrosilylation catalyst. It is not limited especially as such a hydrosilylation catalyst, for example, radical initiators, such as organic peroxide and an azo compound, and a transition metal catalyst are mentioned.

[0029] It is not limited especially as a radical initiator. For example, G t-butyl peroxide, 2, the 5-dimethyl -2, 5-Jl (t-butylperoxy) hexane, 2, the 5-dimethyl -2, 5-Jl (t-butylperoxy)-3-hexyne, Dialkyl peroxide like dicumyl peroxide, t-butyl cumyl peroxide, alpha, and alpha'-bis(t-butylperoxy) isopropylbenzene, Benzoyl peroxide, p-chloro benzoyl peroxide, m-chloro benzoyl peroxide, 2, 4-dichlorobenzoyl peroxide, diacyl peroxide like lauroyl peroxide, Peroxy-acid ester like perbenzoic acid-t-butyl, fault Jl carbonic acid diisopropyl, Peroxi dicarbonate [like fault Jl carbonic acid G 2-ethylhexyl], 1, and 1-Jl (t-butylperoxy) cyclohexane, 1, and 1-Jl (t-butylperoxy) - Peroxy ketal like a 3, 3, and 5-trimethyl cyclohexane etc. can be mentioned.

[0030] Moreover, a complex with the thing which it is not limited [thing] especially as a transition metal catalyst, for example, made support, such as a platinum simple substance, an alumina, a silica, and carbon black, distribute a platinum solid-state, chloroplatinic acid, chloroplatinic acid, alcohol, an aldehyde, a ketone, etc., a platinum-olefin complex, and a platinum (0)-diaryl tetramethyl disiloxane complex are mentioned. As an example of catalysts other than a platinum compound, RhCl (PPh3)3, RhCl3, RuCl3, IrCl3, FeCl3, AlCl3, PdCl2 and H2O, NiCl2, and TiCl4 grade are mentioned. These catalysts may be used independently, and it does not matter even if it uses two or more kinds together. Although there is especially no limit as an amount of catalysts, it is good for using in the range of 10-1 to ten to 8 mol to use in the range of 10-3 to ten to 6 mol often and preferably to one mol of alkenyl radicals of the (B) component. If fewer than ten to 8 mol, hardening will not fully advance. Moreover, since the hydrosilylation catalyst is expensive, it is desirable not to use ten - one or more mols. A platinum allyl compound siloxane is [among these] the most desirable in respect of compatibility, bridge formation effectiveness, and scorching stability.

[0031] Moreover, for radical crosslinking, it is desirable to make a catalyst share. As a catalyst, radical initiators, such as organic peroxide, are used as a catalyst. It is not limited especially as a radical initiator. For example, G t-butyl peroxide, 2, the 5-dimethyl -2, 5-Jl (t-butylperoxy)

hexane, 2, the 5-dimethyl -2, 5-Jl (t-butylperoxy)-3-hexyne, Dialkyl peroxide like dicumyl peroxide, t-butyl cumyl peroxide, alpha, and alpha'-bis(t-butylperoxy) isopropylbenzene, Benzoyl peroxide, p-chloro benzoyl peroxide, m-chloro benzoyl peroxide, 2, 4-dichlorobenzoyl peroxide, diacyl peroxide like lauroyl peroxide, Peroxy-acid ester like perbenzoic acid-t-butyl, fault Jl carbonic acid diisopropyl, Peroxi dicarbonate [like fault Jl carbonic acid G 2-ethylhexyl], 1, and 1-Jl (t-butylperoxy) cyclohexane, 1, and 1-Jl (t-butylperoxy) - Peroxy ketal like a 3, 3, and 5-trimethyl cyclohexane etc. can be mentioned. 2, the 5-dimethyl 2, a 5-Jl (tert-butylperoxy) hexane, 2, the 5-dimethyl 2, and 5-Jl (tert-butylperoxy) hexyne-3 are [among these] desirable in respect of odor nature, coloring nature, and scorching stability.

[0032] The loadings of organic peroxide have the desirable range of 0.5 - 5 weight section to the isobutylene system block-copolymer 100 weight section at the time of addition of organic peroxide.

[0033] The constituent of this invention can blend the bridge formation assistant which has an ethylene system partial saturation radical on the occasion of the bridge formation processing by organic peroxide. An ethylene system partial saturation radical is a polyfunctional methacrylate monomer like a divinylbenzene, a polyfunctional vinyl monomer like a triaryl SHIANU rate or ethylene glycol dimethacrylate, diethylene-glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, trimethylolpropanetriethacrylate, and allyl compound methacrylate etc. These may be used independently or may use at least two or more sorts. With such a compound, homogeneity and efficient crosslinking reaction are expectable.

[0034] In order to be easy to deal with ethylene glycol dimethacrylate and triethylene glycol dimethacrylate, to have a peroxide solubilization operation and to work as a distributed assistant of peroxide also especially in it, since the homogeneity and bridge formation thermoplastic elastomer which was effective and was able to balance hardness and rubber elasticity is obtained, the bridge formation effectiveness by heat treatment is desirable.

[0035] Below 20 weight sections of the addition of the above-mentioned bridge formation assistant are desirable to the isobutylene system (polymer B) 100 weight section which has an alkenyl radical at the end. When 20 weight sections are exceeded, there is an inclination for independent gelation of a bridge formation assistant to tend to progress, and there is a problem in respect of cost.

[0036] In the constituent of this invention, in order to raise reinforcement further in addition to an isobutylene system block copolymer (A) and the isobutylene system polymer (B) which has an alkenyl radical at the end, reinforcing materials (C) may be added further. The resin for reinforcement with which *** consists [using inorganic bulking agents, carbon black, etc., such as the resin for reinforcement, such as polyphenylene ether, polystyrene, and those constituents, a calcium carbonate, talc, a mica, a kaolin, a silica, and a glass fiber,] of polyphenylene ether, polystyrene, and those constituents as reinforcing materials (C) is desirable. These can use one or more sorts. By reinforcing materials' addition, the tensile strength of a thermoplastic-elastomer constituent improves, and a compression set also improves depending on the class of loadings or reinforcing materials. Moreover, the demand characteristics further doubled with each application at the constituent of this invention are accepted. In the range which does not spoil physical properties, a plasticizer and a bulking agent, for example, a styrene-butadiene-styrene block copolymer (SBS) and a styrene-isoprene-styrene block copolymer (SIS). Moreover, elastomers, such as a styrene-ethylene butylene-styrene block copolymer (SEBS) which hydrogenated them, and a styrene-ethylene propylene-styrene block copolymer (SEPS). Polyphenylene ether, polystyrene, PPO, a polyphenylene ether-polystyrene constituent. In addition to this, the antioxidant of a hindered phenol system or a hindered amine system, an ultraviolet ray absorbent, light stabilizer, a pigment, a surfactant, a reaction retarder, a flame retarder, a bulking agent, a reinforcing agent, etc. can be blended suitably.

[0037] The straight mineral oil used as a plasticizer in the case of processing of rubber - or liquefied or the synthetic softener of low molecular weight can be used. As straight mineral oil, although the high-boiling point petroleum component of paraffin series, a naphthene, and an aromatic series system is mentioned, the paraffin series and the naphthene which do not check crosslinking reaction are desirable. As liquefied or a synthetic softener of low molecular weight.

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although there is especially no limit, polybutene, hydrogenation polybutene, liquid polybutadiene, hydrogenation liquid polybutadiene, and the Porl alpha olefins are mentioned. These plasticizers can use one or more sorts. As for the loadings of a plasticizer, it is desirable that it is the 10 - 300 weight section to the isobutylene system (polymer B) 100 weight section in which the alkenyl radical was introduced into the end. If loadings exceed the 300 weight sections, a problem will arise in a fall and moldability of a mechanical strength. As most desirable constituent of the thermoplastic-elastomer constituent of this invention isobutylene system (polymer B) 10-300 by which the alkenyl radical was introduced into the end to the isobutylene system block-copolymer (A) 100 weight section - weight - the section - Preferably to reinforcing materials (C) 0 - the 100 weight sections, and a pan an isobutylene - a system - a block copolymer - (A -) - 100 - weight - the section - receiving - an end - the alkenyl - a radical - introducing - having had - an isobutylene - a system - a polymer - (B -) - 50 - 150 - weight - the section - reinforcing materials - (C -) - zero - 50 - weight - the section - and - a cross linking agent - (D -) - having blended - a constituent - it is . In this case, to the denaturation isobutylene system block-copolymer (B) 100 weight section in which the alkenyl radical was introduced into the end, a cross linking agent (D) is 0.01 - 20 weight section, and a bridge formation assistant has desirable 0 - 20 weight section.

[0038] Moreover, especially the manufacture approach of the thermoplastic-elastomer constituent of this invention is not limited, but if an isobutylene system block copolymer (A), the isobutylene system polymer (B) with which the alkenyl radical was introduced into the end, and the above-mentioned component used by the case are the approaches which may be mixed by homogeneity, it can adopt all.

[0039] When constructing a bridge dynamically in the isobutylene system polymer (B) with which the alkenyl radical was introduced into the end and manufacturing the thermoplastic-elastomer constituent of this invention at the time of melting mixing of an isobutylene system block copolymer (A) and the isobutylene system polymer (B) with which the alkenyl radical was introduced into the end, it can carry out preferably by the approach of illustrating below.

[0040] For example, when manufacturing using direct-vent-system kneading equipment or batch type kneading equipments, such as a lab PURASUTO mill, Brabender, a Banbury mixer, a kneader, and a roll, melting kneading can be carried out until it mixes beforehand all components other than a cross linking agent and a bridge formation assistant, and a bridge formation catalyst and becomes homogeneity, and the approach of adopting how a cross linking agent and a bridge formation assistant, and a bridge formation catalyst are added subsequently to it, and crosslinking reaction fully stops melting kneading can be adopted.

[0041] Moreover, when manufacturing using the melting kneading equipment of continuous system like a single screw extruder and a twin screw extruder it pelletsizes, after carrying out melting kneading of all the components other than a cross linking agent and a bridge formation assistant, and a bridge formation catalyst until it becomes homogeneity with melting kneading equipments, such as an extruder, beforehand. After carrying out the dryblend of a cross linking agent and a bridge formation assistant, and the bridge formation catalyst to the pellet, melting kneading is further carried out with melting kneading equipments, such as an extruder. How to manufacture the thermoplastic-elastomer constituent which constructs a bridge dynamically in an isobutylene system polymer, and consists of a bridge formation object of the isobutylene system block copolymer (A) of this invention, and the isobutylene system polymer (B) with which the alkenyl radical was introduced into the end. Or melting kneading of all the components other than a cross linking agent (D) and a bridge formation assistant, and a bridge formation catalyst is carried out with melting kneading equipments, such as an extruder. Add a cross linking agent and a bridge formation assistant, and a bridge formation catalyst from the middle of the cylinder of an extruder there, and melting kneading is carried out further. A bridge is dynamically constructed in the isobutylene system polymer (B) with which the alkenyl radical was introduced into the end. The approach of manufacturing the thermoplastic-elastomer constituent which consists of a bridge formation object of the isobutylene system block copolymer (A) of this invention and the isobutylene system polymer (B) with which the alkenyl radical was introduced into the end etc. is employable.

[0042] In performing the above-mentioned method of performing dynamic bridge formation to melting kneading and coincidence, 150-210-degree-C temperature is desirable.

[0043] The bridge formation object of the isobutylene system polymer (B) with which the alkenyl radical was beforehand introduced into the end is manufactured, and when mixing the bridge formation object with an isobutylene system block copolymer (A) and adjusting the thermoplastic-elastomer constituent of this invention, the approach of illustrating below is adopted preferably.

[0044] To the isobutylene system polymer (B) with which the alkenyl radical was introduced into the above-mentioned end, for example, a cross linking agent and a bridge formation assistant. Add a bridge formation catalyst and it fully kneads at suitable temperature using the kneading machine usually used for manufacture of a rubber bridge formation object. After adopting suitable bridge formation temperature and bridge formation time amount for the obtained kneading object using the press machine etc. and advancing crosslinking reaction. The bridge formation object of the isobutylene system polymer (B) with which it ground after cooling and the alkenyl radical was introduced into the end can be obtained, and the thermoplastic-elastomer constituent of this invention can be manufactured by carrying out melting mixing of the bridge formation object with an isobutylene system block copolymer (A).

[0045] any of the known approach currently conventionally used for manufacture of thermoplastics or a thermoplastic-elastomer constituent as melting alligation of the bridge formation object of the isobutylene system polymer (B) with which the alkenyl radical was introduced into the end on that occasion, and an isobutylene system block copolymer (A) - although - it can adopt, for example, can carry out using a lab PURASUTO mill, a Banbury mixer, a single screw extruder, a twin screw extruder, and other melting kneading equipments, and melting kneading temperature has desirable 150-210 degrees C.

[0046] The thermoplastic-elastomer constituent of this invention can be fabricated using the molding approach and shaping equipment which are generally adopted to a thermoplastics constituent, for example, can carry out melting shaping by extrusion molding, injection molding, press forming, blow molding, etc. Moreover, since it excels in the moldability and the compression set property, the thermoplastic-elastomer constituent of this invention can be effectively used as the sound deadener for light electric appliance dexterous dampers, such as seal material, such as a packing material, a sealant, a gasket, and a plug, and CD damper, a structural damper, an automobile, a car, and home electronics etc., a vibroisolating material, automobile interior material, a cushioning material, daily necessities, an electrical part, electronic parts, a sport member, a grip or shock absorbing material, wire covering material a packing material, various containers, and stationary components.

[0047]

[Example] Although this invention is further explained below at a detail based on an example, this invention does not receive a limit at all by these. In addition, in advance of an example, various measuring methods, an appraisal method, and an example are explained.

[0048] (Degree of hardness) Based on JIS K 6352, the test piece used 12.0mm ** press sheet.

[0049] (*** breaking strength) Based on JIS K 6251, the test piece pierced and used 2mm thickness press sheet for the No. 3 mold by the dumbbell. The speed of testing was considered as a part for 500mm/.

[0050] (*** elongation after fracture) Based on JIS K 6251, the test piece pierced and used 2mm thickness press sheet for the No. 3 mold by the dumbbell. The speed of testing was considered as a part for 500mm/.

[0051] (Compression set) Based on JIS K 6262, the test piece used 12.0mm thickness press sheet. It measured on condition that deformation 70 degree-Cx 22 hours, and 25%.

[0052] (Dynamic viscoelasticity) JIS Based on K-6394 (vulcanized rubber and dynamic property test method of thermoplastic rubber), the test piece with a 5mm(6mm by) x thickness of 2mm was cut down, and loss tangent tandelta was measured using dynamic viscoelasticity measuring device DVA-200 (T measurement control company make). The test frequency could be 0.05Hz.

[0053] Moreover, the cable address and the concrete contents of the ingredient used for below in the example and the example of a comparison are shown.

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi.ejje

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SIBS: Polystyrene-polyisobutylene-polystyrene triblock copolymer APIB: Polyisobutylene by which the allyl group was introduced into the end EP600A IIR by Kaneka Co., Ltd.: Isobutylene isoprene rubber, product made from JSR (trade name "Butyl065")

Reinforcing materials: P PO Noryl EFN4230 (Japanese G IPU latic incorporated company make)

Cross-linking-agent 1: The chain-like siloxane cross linking agent 2 which contains an average of five hydrosily radicals and an average of five alpha-methylstyrene radicals in a molecule: A reaction type bromination alkylphenol formaldehyde compound, Taoka Chemical Co., Ltd. make (trade name "the tacky roll 250-1")

Bridge-formation assistant 1: Triethylene glycol dimethacrylate, new Nakamura chemistry company make (trade name "NK ester 3G")

Bridge-formation Assistant 2: Zinc-oxide bridge-formation catalyst: 1, 1 and 3 of zerovalent platinum, 3-tetramethyl - 1, 3-diaryl disiloxane complex 1% xylene solution.

[0054] (Example 1 of a manufacture) Manufacture of a styrene-isobutylene-styrene block copolymer (SIBS)

A syringe is used after carrying out the nitrogen purge of the inside of the polymerization container of the separable flask of 2L, n-hexane (what was dried by molecular sieves) 456.4mL, and butyl chloride (what was dried by molecular sieves) 656.3mL are added. After attaching a polymerization container all over -70-degrees C dry ice / methanol bus and cooling. The liquid-sending tube made from Teflon (trademark) was connected to proof-pressure glass liquefaction extraction tubing with a three-way cock containing isobutylene monomer 232mL (2871mmol), and the isobutylene monomer was sent by nitrogen pressure in the polymerization container. p-JIKUMIRU chloride 0.847g (2.8mmol) and 1.22g (14mmol) of N,N-dimethylacetamide were added. Next, titanium-tetrachloride 8.67mL (79.1mmol) was added further, and the polymerization was started. After agitating at the temperature same for 2.5 hours from polymerization initiation, polymerization solution abbreviation 1mL was sampled as an object for a sampling from the polymerization solution. Then, the mixed solution of styrene monomer 77.9g (748mmol) beforehand cooled at -70 degrees C, n-hexane 14.1mL, and butyl chloride 20.4mL was added in the polymerization container. In addition to a lot of water, the reaction was terminated 2 hours after adding this mixed solution.

[0055] The reaction solution was rinsed twice, the solvent was evaporated and the target block copolymer was obtained by carrying out the vacuum drying of the obtained polymer at 60 degrees C for 24 hours. The molecular weight of the polymer obtained by the gel-permeation-chromatography (GPC) method was measured. The block copolymer whose Mw of a block copolymer is 101,000 was obtained.

[0056] (Example 1) With SIBS manufactured in the example 1 of manufacture, and the rate which showed APIB in Table 1, melting kneading was carried out for 5 minutes using the lab PURASUTO mill (Oriental energy machine company make) set as 150 degrees C, and infanticide continuation kneading was added and carried out for 5 minutes at a rate which showed the cross linking agent subsequently to Table 1. The bridge formation catalyst was supplied, melting kneading was carried out further, and dynamic bridge formation was performed. The obtained thermoplastic-elastomer constituent was able to be easily fabricated at 180 degrees C in the shape of a sheet. The degree of hardness, the **** breaking strength, the **** elongation after fracture and the compression set of the obtained sheet, and dynamic viscoelasticity were measured according to the above-mentioned approach. A result is shown in Table 1.

[0057] (Example 2) It mixed at a rate which showed SIBS, APIB, and reinforcing materials in Table 1, and dynamic bridge formation as well as an example 1 was performed. The obtained thermoplastic-elastomer constituent was able to be easily fabricated at 180 degrees C in the shape of a sheet. The degree of hardness, the **** breaking strength, the **** elongation after fracture, and the compression set of the obtained sheet were measured according to the above-mentioned approach. A result is shown in Table 1.

[0058] (Example 1 of a comparison) After carrying out melting kneading for 10 minutes using the lab PURASUTO mill which set SIBS manufactured in the example 1 of manufacture as 180 degrees C, it fabricated at 180 degrees C in the shape of a sheet. The degree of hardness of the obtained sheet, **** breaking strength, **** elongation after fracture, and a compression set

were measured according to the above-mentioned approach. A result is shown in Table 1.

[0059] (Example 2 of a comparison) SIBS manufactured in the example 1 of manufacture, and IIR at a rate shown in Table 1 Melting kneading was further carried out at 180 degrees C, and dynamic bridge formation was performed until it carried out melting kneading for 5 minutes using the lab PURASUTO mill (Oriental machine company make) set as 180 degrees C, it added at a rate which, subsequently to Table 1, showed the cross linking agent 2, the bridge formation assistant 3, and the bridge formation assistant 4 and the value of torque showed the peak price (3 - 7 minutes). The obtained thermoplastic-elastomer constituent was able to be easily fabricated at 180 degrees C in the shape of a sheet. The degree of hardness, the **** breaking strength, the **** elongation after fracture, and the compression set of the obtained sheet were measured according to the above-mentioned approach. A result is shown in Table 1.

[0060] (Example 3 of a comparison) The constituent was created like the example 1 at a rate shown in Table 1 using APIB. However, a sheet-like Plastic solid was not able to be acquired using this constituent.

[0061] (Example 4 of a comparison) The sheet was created using Mitsubishi Chemical RABARON SJ5400N, and a degree of hardness, **** breaking strength, **** elongation after fracture and a compression set, and dynamic viscoelasticity were measured according to the above-mentioned approach. A result is shown in Table 1.

[0062]

[Table 1]

試料名	比較例 1 実例 1 比較例 2 比較例 3				試験方法
	1	2	3	4	
SIBS (重量比)	100	100	100	100	三井化学株式会社
APIB (重量比)	100	180		100	ラボン
IIR (重量比)			100		SJS400N
橋形成剤 (重量比)		18			
橋形成剤 1 (重量比)	9	26			6
橋形成剤 2 (重量比)			10		
橋形成剤 3 (重量比)				5	
橋形成剤 4 (重量比)			1		
架橋剤 (重量比)	ASO	800		25	
架橋剤 (重量比)	ASO	800		25	
硬度 (JIS A)	36	43	50	36	シートに成形できない
引張強さ (MPa)	4.9	6.5	15.9	6.1	A.5
引張伸び (%)	720	282	876	490	784
圧縮永久変形 (%)	62	44	68	68	23
tan δ (-30°C)	1.21	-	1.22	-	6.2
tan δ (30°C)	0.19	-	0.21	-	6.23

比較例 3 の架橋剤は APIB 100g に対して加えた量

[0063] The thermoplastic-elastomer constituent of this invention has the value of a compression set lower than the SIBS simple substance which is an isobutylene system block copolymer shown in the example 1 of a comparison, and it excels in the compression set, with the property of an isobutylene system block copolymer held. And though a degree of hardness is comparable or soft as compared with the case where IIR is used for the bridge formation object shown in the

example 2 of a comparison, excelling in the value of a compression set is clear. Moreover, as compared with the example 4 of a comparison, it is clear that the thermoplastic-elastomer constituent's of an example 1 the value of tandelta is highly excellent in vibration-deadening nature.

[0064]

[Effect of the invention] Thus, a thermoplastic-elastomer constituent is a new thermoplastic-elastomer constituent which was rich in flexibility and was excellent in fabrication nature, a rubber-property, a mechanical strength, a compression set property, and vibration-deadening nature, with the property of an isobutylene system block copolymer held.

[Translation done.]